

Oxidative dehydrogenation of ethylbenzene over La and Dy supported vanadia

S Sugunan* & N K Renuka

Department of Applied Chemistry,
Cochin University of Science and Technology,
Kochi 682 022, India

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A series of supported vanadia systems have been prepared by excess solvent technique using La_2O_3 and Dy_2O_3 as supports. Physical characterization has been carried out using XRD, FTIR, TG studies, BET surface area measurement, pore volume analysis etc. Cyclohexanol decomposition has been used as a test reaction for evaluating the acid base properties of the supported system. The oxidative dehydrogenation of ethylbenzene has been employed as a chemical probe reaction to examine the catalytic activity. The active species correspond to amorphous and crystalline tetrahedral vanadyl units in the supported system.

Vanadium pentoxide and related phases are of great importance in industrial catalysis and have been extensively used as neat oxides or in supported forms. A large quantum of research work has been devoted to provide insight into the nature and reactivity of supported vanadia catalysts¹⁻⁴. The basic and amphoteric oxides favour the bidimensional dispersion (often with the formation of compounds), whereas acidic supports favour^{1,2} three-dimensional micro units of V_2O_5 . Earlier studies on supported vanadia catalysts indicated that it is mainly used in oxidative dehydrogenation reactions⁵⁻⁷. Recently, there has been a strong interest to study the oxidative dehydrogenation of ethylbenzene, owing to the potential commercial importance of styrene. Generally attempted catalytic systems for the reaction include metal oxides, phosphates and organic polymers. Among the transition metal oxides, V-Mg-O system is by far the most active and selective catalyst for the preparation of styrene⁸. Two possible types of catalysis have been proposed for the above reaction: one depends on the redox operation of the transition metal oxide⁹ and the other involves catalytically active coke¹⁰.

It has been well established that, the oxidative dehydrogenation (ODH) reactions proceed well with commendable selectivity, when vanadia is supported

on basic metal oxides¹¹. The present study demonstrates the effect of supporting vanadia on La_2O_3 and Dy_2O_3 in the oxidative dehydrogenation. Only limited studies have been reported in this area, which were restricted to the ODH reactions of alkanes¹². Ln/V systems prepared by wet impregnation method were characterized and were evaluated for the catalytic activity towards oxidative dehydrogenation of ethyl benzene. The nature of the active vanadia species was also discussed.

Experimental

Rare earth oxide supports, La_2O_3 and Dy_2O_3 were obtained from nitrate solution by precipitation via hydroxide method, using ammonia. Supported vanadia systems were prepared by wet impregnation method as reported earlier, by stirring an aqueous oxalic acid solution of NH_4VO_3 with Sm_2O_3 followed by evaporation and calcination at 450°C for six hours. The following compositions of V_2O_5 were selected in the present study, namely 3, 7, 11 and 15 wt % of vanadia which were denoted as Ln3, Ln7, Ln11 and Ln15 respectively (Ln = rare earth metal). The samples were powdered below 100 mesh size and activated at 500°C for two hours prior to each experiment.

The crystallinity of the catalysts was determined by the powder XRD method by a Rigaku D-max C X-ray diffractometer using Ni filtered Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$). The FTIR spectra of the samples were recorded in a Shimadzu spectrophotometer (DR 8001) in the range $4000\text{-}400 \text{ cm}^{-1}$. Surface areas of the catalysts were measured using a Micromeritics Flowprep Surface area analyser by low temperature nitrogen adsorption method. Measurements of pore volume and pore size distribution of the catalysts were carried out using Quantachrome, Auto scan-92 porosimetry (USA). The thermal stability of the system was examined using a Shimadzu thermogravimetric analyser (TGA-50) in nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$.

For probing acid base property, cyclohexanol decomposition was carried out in vapour phase at 350°C with 2.5 g catalyst. The products were analysed by GC fitted with a $6' \times 1/8$ stainless steel column packed with 5 % NPQSB + H_3PO_4 on anachrom A 80 / 100 mesh.

The oxidative dehydrogenation reaction was performed in a vapour phase downflow silica reactor. Before each experiment, the catalyst was activated in a current of dry air at 500°C and then brought to reaction temperature in presence of nitrogen flow. Ethylbenzene was then introduced into the carrier stream from a saturator containing liquid ethylbenzene. The mass balance was noted each time and liquid products were analysed using a Shimadzu GC-15 A gas chromatograph fitted with a xylene master capillary column and FID.

Results and discussion

The physical and chemical characteristics of the catalysts are given in Table 1. XRD patterns indicated the formation of lanthanide orthovanadates in the supported systems, along with pure rare earth oxides. Pure La_2O_3 exhibited prominent XRD peaks at 2θ values 29.95, 46, 39.95, 52.13 and 26.12° and their corresponding d spacing values are 2.98, 1.96, 2.28, 1.75 and 3.41 Å (Fig. 1). When supported with vanadia, peaks were observed at 27.75, 26.15, 30.05, 46.55 and 28.95° and d spacings were 3.21, 3.41, 2.97, 1.94 and 23 Å respectively, which correspond to LaVO_4 peaks arising from Dy_2O_3 were detected at 2θ values 28.9, 14.30, 33.4, 20.21 and 33.6° (values were 3.08, 1.88, 2.67, 4.35 and 2.66 Å respectively) (Fig. 2). The vanadia supported analogues exhibited reflections at 24.9, 33.35, 49.5, 18.6 and 35.45°, with d spacings 3.57, 2.68, 1.83, 4.76 and 2.53 Å respectively. Pure crystalline V_2O_5 gave important peaks at values 20.2, 26.2, 31, 18.4 and 33.6° (Fig. 3). Their d spacings were 4.38, 3.40, 2.88, 5.76 and 2.61 Å respectively. A comparison of these values shows that crystalline V_2O_5 is not there in the supported catalysts even at higher wt % of vanadia. This is in agreement with the views of Corma *et al.*¹² that basic oxides preferably form compounds with vanadia. The relative intensity of the

respective orthovanadate peaks increased with increase in vanadia content in the sample as evident from the relative heights of the characteristic peaks corresponding to different components. FTIR spectra shown in Fig. 4 agree well with these observations. The broad band ~ 800 cm^{-1} region was identified as that of LnVO_4 species. Besides, the characteristic band of V_2O_5 is not observed in the spectrum of the supported samples at 1020 cm^{-1} , confirming the results of XRD studies. Amorphous vanadia bands were located at 1060 and 1065 cm^{-1} region for La/V and Dy/V systems respectively. The slight difference in the band position is justified by the higher electronegativity of Dy ion compared to La ion. The fact that only one frequency of V=O vibration is observed leads to the absence of O=V=O fragments on the surface species¹³. As shown by Frederickson and Hausen, crystalline poly vanadates manifest V=O stretching frequencies in the 1000 – 950 cm^{-1} region¹⁴ and the comparatively high value in the present case rules out their presence on the surface. These surface vanadia species were assigned a tetrahedral geometry, as confirmed by earlier studies¹⁵⁻¹⁷. The intensity of the bands in the hydroxyl region is decreased for supported system indicating the participation of surface hydroxyls in bond formation with vanadia. Besides, there is a shift for the region of the band to lower frequency. The IR

Table 1—Physico chemical characteristics of rare earth oxide supported vanadia systems

Catalyst	BET S. A (m^2/g)	Pore volume (cm^3/g)	Selectivity (%)	
			Cyclohexene	Cyclohexanone
La_2O_3	45.23	1.06	40.90	59.10
La3	35.13	1.11	87.74	12.26
La7	32.13	1.01	88.37	11.63
La11	40.53	1.40	86.48	13.52
La15	48.16	0.86	82.27	18.73
Dy_2O_3	21.99	0.83	30.12	69.88
Dy3	26.09	0.90	87.29	12.71
Dy7	23.29	0.78	87.46	12.54
Dy11	18.71	0.68	87.48	12.52
Dy15	18.01	0.65	80.14	11.86

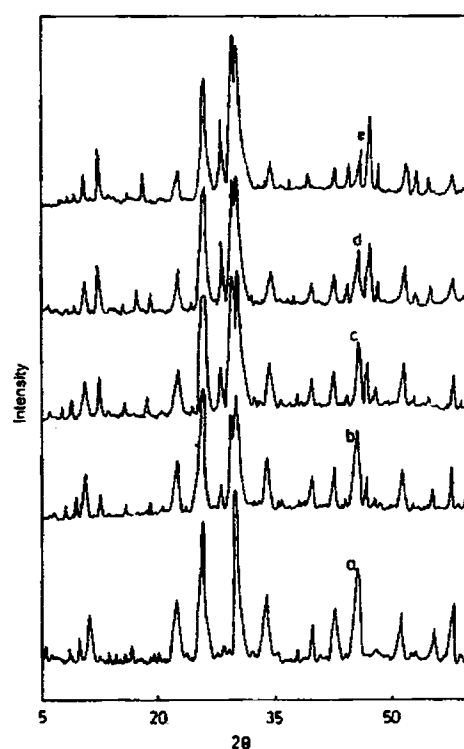


Fig. 1—XRD patterns of the catalysts a) La_2O_3 ; b) La3; c) La7; d) La11; e) La15

band at higher frequency has been assigned to the most basic hydroxyl group and the shift to lower frequency indicates the increased acidity of the OH groups¹⁸.

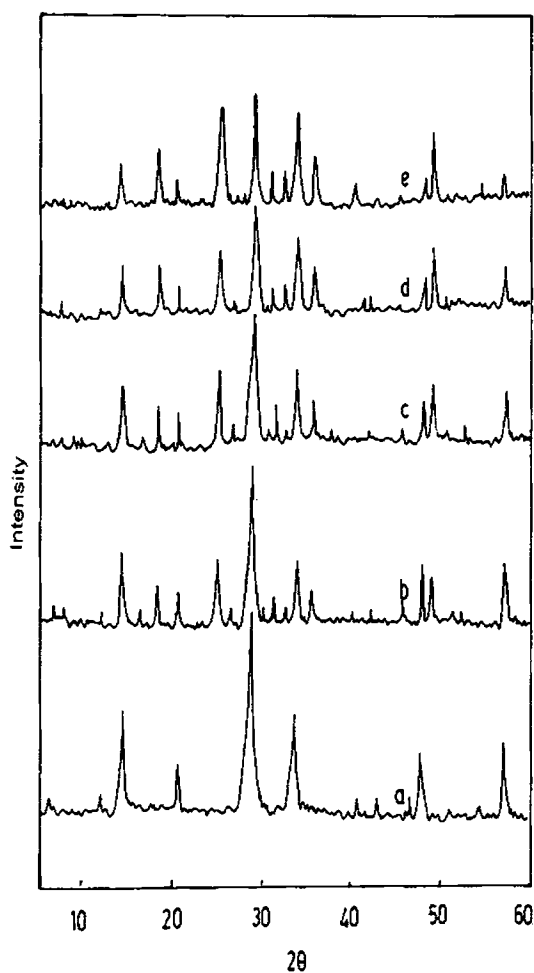


Fig. 2—XRD patterns of the catalysts a) Dy_2O_3 ; b) Dy_3 ; c) Dy_7 ; d) Dy_{11} ; e) Dy_{15}

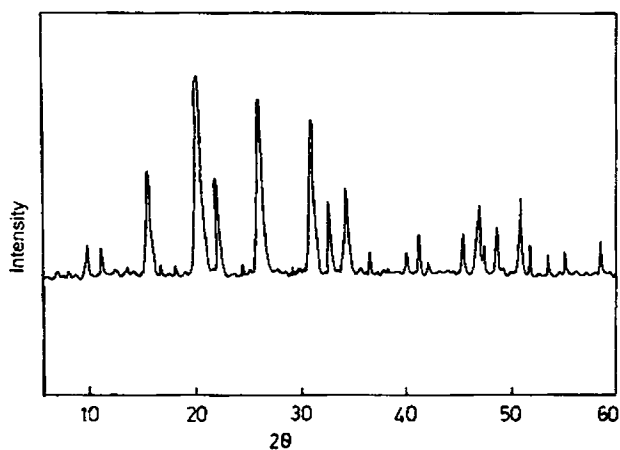


Fig. 3—XRD pattern of V_2O_5

Hence, it can be presumed that, the surface vanadia species coordinate to the oxide support by titrating the basic surface hydroxyls of the support. Pore volume distribution curves obtained by mercury porosimeter revealed a decrease of macropores and a shift of the major pores to mesoporous region by the addition of vanadia. The formation of crystalline vanadate at 450°C was confirmed by thermogravimetric studies and the supported system was found to be stable to 800°C .

Cyclohexanol decomposition is the conventionally used probe reaction for acid base property studies. The amphoteric character of the alcohols permits their interaction with acidic and basic sites of the catalyst, leading to dehydration and dehydrogenation products. Dehydration of cyclohexanol leads to cyclohexene, which is attributed to the presence of Bronsted acid sites of the catalysts¹⁹. Dehydrogenation that leads to cyclohexanone formation is taking place by the combined participation of acid and base sites²⁰. As a result, dehydrogenation rate is proportional to both acidity and basicity. For pure rare earth oxides, dehydrogenation is prominent which leads to cyclohexanone in major amount indicating strong basic sites on the catalyst (Table 1). For supported vanadia systems, dehydration products predominate, as seen from the enhanced selectivity of cyclohexene. This in turn indicates that the Bronsted acid sites are increasing upon vanadia incorporation, which is in agreement with earlier reports^{21,22}. Turek *et al.* proposed that, Bronsted acidity in the case of supported catalysts is located at Support-O-V bonds, even though no spectroscopic

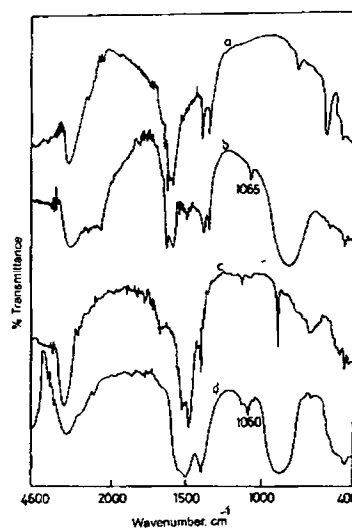


Fig. 4—FTIR spectra of the catalysts a) Dy_2O_3 b) Dy/V c) La_2O_3 d) La/V

evidences exists in favour of this²³. It can be seen that no remarkable increase for the yield of cyclohexene is observed at V_2O_5 % > 3. Contribution of vanadia to surface species may be less after 3wt%, where predominant formation of lanthanide orthovanadate occurs. Apart from this, the decrease of Lewis acid and base sites is also evident by the decrease in the concentration of cyclohexanone.

Data on oxidative dehydrogenation of ethylbenzene are presented in Table 2. Along with styrene, small amount of benzene and toluene are also detected among the products as a result of the interaction of ethylbenzene with the acid and base sites of the catalysts. Carbon oxides are the other products, which were formed by the complete oxidation of the organics. As seen from Table 2, pure vanadia exhibited more than 80% selectivity towards carbon oxides. Carbon oxide selectivity of pure La_2O_3 was also high. From the results, it is obvious that, the selective oxidation activity of ethylbenzene to styrene is greatly influenced by supporting vanadia. Comparing the two systems, Dy/V system exhibited higher selectivity and activity. Styrene selectivity was found to be independent of percentage conversion of ethylbenzene. Almost constant selectivity was detected for the two systems at higher vanadia loadings.

According to Tagawa *et al.*²⁴, the acid sites of Hammett H_o values between 1.5 and -5.6 are found to be the active sites for ethylbenzene conversion, which adsorb ethylbenzene reversibly. Oxidation of the same occurs on the basic sites of pK_a lying between 17.2 and 26.5. The tendency to have maximum activity suggests the cooperative effect of the acid base properties of the catalyst. However, in the rare earth oxide supported

vanadia systems, no such sites were detected by Hammett indicator method. So the influence of acid base properties on the selective oxidation activity will be negligible here. According to earlier reports the catalytic behaviour of vanadium based systems in selective oxidation strongly depends on the redox property of the vanadium species as well as on the acid base character of support and catalyst^{25,26}. So apart from the acidic basic properties, the redox property plays an important role in ODH reaction of ethylbenzene.

The role of vanadia in developing selective oxidation activity to styrene on rare earth supports is apparent from the data in Table 2. According to Sachtler *et al.*, the selectivity in oxidation reaction is determined by two factors; i) by the intrinsic activity of lattice oxygen and ii) by their availability^{27,28}. If only a limited number of lattice oxygen is available, oxidation stops at a particular level to result in partial oxidation products. Abstraction of too many hydrogen will lead to breaking of C - C bond resulting in total oxidation products. In the supported systems, there is no large reservoir of bulk oxygen that is available to abstract so many oxygens. Thus the locally limited amount of reactive lattice oxygen might be the explanation for selective oxidation activity. Pure rare earth oxides also catalyses complete oxidation of the organics. Lanthanide oxides possess low binding energy which will make the lattice oxygen highly mobile²⁹. So oxygen insertion takes place in the partial oxidation products resulting in carbon oxides.

The locally limited active oxygen in the case of supported systems can be justified as follows. The activity for partial oxidation of the supported system is related to the coordination environment of vanadium ion in the catalysts. Two types of vanadia species were detected in Ln / V systems, surface vanadia species and lanthanide orthovanadates, which consists of tetrahedral vanadyl units. Isolated tetrahedral V^{5+} species are proven to be active and selective centers for oxidative dehydrogenation reactions³⁰⁻³². Enhancement of selectivity by tetrahedral vanadium is connected with the availability of the lattice oxygen at the reaction site apart from the nucleophilicity of lattice oxygen. This oxygen availability is expressed as the average number of oxygen molecules that react with each hydrocarbon molecule, known as average oxygen stoichiometry (AOS)³⁰. The number of vanadyl units that can effectively interact with the adsorbed hydrocarbon unit determines the AOS in the case of a particular system.

Table 2—Oxidative dehydrogenation of ethylbenzene over La / V system [Reaction conditions: Reaction temperature= 475°C; feed rate= 6 ml/h; catalyst= 2 g; time on stream= 1 h; air flow rate= 20 ml/min.]

Catalyst	Conversion (%)	Selectivity (%)			
		Styrene	Toluen e	Benzene	C-oxides
V_2O_5	35.8	5.2	1.6	3.0	90.2
La_2O_3	18.5	42.1	5.9	2.2	49.8
La3	16.5	65.1	4.1	2.0	28.8
La7	15.6	71.8	2.7	0.7	25.3
La11	13.0	70.3	2.3	1.6	24.8
La15	14.4	71.9	2.3	3.8	21.7
Dy3	15.5	85.0	2.3	1.7	11.0
Dy7	22.1	90.2	2.0	1.5	6.3
Dy11	23.2	91.2	1.4	0.9	6.5
Dy15	25.2	91.2	1.2	0.5	7.2

The effective size of such a unit is governed both by the size of the reactant and the rate of reoxidation of the active center. In the case of rare earth supported vanadia, VO_4 units are isolated (sufficiently apart), which supplies only a limited number of oxygen atoms to react with hydrocarbon molecule, improving selectivity.

Comparing the two supported analogues, Dy/V Series showed higher styrene selectivity and activity. This is related to the intrinsic activity of surface oxygen. In retrospect, the bonding in M-O-V was suggested to be the primary factor that determines the selectivity in ODH reaction^{33,34}, which decides the intrinsic activity of the surface oxygen. The reducibility of the metal ion in the oxide is thought to be an important factor affecting its activity, i.e., the oxidizing ability of the system. A catalyst that is too difficult to be reduced is too inactive with high selectivity, while that is too easily reduced is active but non selective. So if the vanadate unit is composed of a more reducible ion, the selectivity of ODH product will be low with high activity³⁵. Here, the reducibility of the rare earth ions is in the order, $\text{La} < \text{Dy}$. According to this, La/V system should exhibit low activity with higher selectivity towards styrene. From the results it is apparent that, the selectivity is lower for La/V system.

The unexpected behaviour of La/V systems can be explained as follows. After 'H' abstraction, the partial oxidation product can desorb to gas phase or undergo further reaction with insertion of oxygen to form carbon oxides. The fate of the adsorbed product depends on a) the desorption rate of styrene. i.e., rate of diffusion of the oxygen in the lattice relative to the residence time of organic species on the catalyst surface and b) the number of available lattice oxygen in the vicinity and the mobility of oxygen. i.e., mobility of oxygen which helps to replenish the oxygen vacancies formed on oxidation. Residence time of the product on the surface before desorption is an important factor which controls the selectivity of the products. This is dependent on the nature of adsorbate; an acidic product formed will be easily desorbed from an acidic catalyst, and a basic one get easily detached from a basic surface. Styrene being basic is less strongly bound and thus more easily desorbed from a catalyst, which shows higher basicity. As far as this factor is considered, the selectivity of styrene is expected to be high for the La/V series. But here, the second factor, that is the replenishment of lattice oxygen or the mobility, may be the significant contributing factor, which in turn leads to products with

higher number of oxygen that eventually result in more percentage of carbon oxides. It has been reported that, the rare earths possess low binding energy for lattice oxygen. Lattice oxygen binding energy is lower for La^{29} . More mobile lattice oxygen leads to higher degree of oxidation leading to complete combustion products on La / V samples. So the selectivity follows the order $\text{Dy} / \text{V} > \text{La} / \text{V}$.

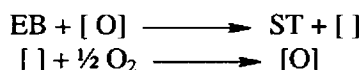
Data given in Table 2 show that, above 7% vanadia, styrene selectivity was almost constant. Here this behaviour is supposed to be due to the formation of lanthanide orthovanadate, which may be forming predominantly after 7% vanadia. This can be explained as follows. Taking the surface area of vanadyl unit as 16 \AA^2 , it can be seen that the monolayer coverage of the surface by vanadia is over by 7 wt% approximately. Further vanadia addition may be mainly contributing to crystalline SmVO_4 formation. Hence up to 7 % V_2O_5 , surface species may be contributing to styrene selectivity. At higher vanadia concentration, vanadates have a prominent role, which exhibits a constant selectivity towards styrene. Chang *et al.* reported a similar observation with magnesium orthovanadate, which exhibits constant styrene selectivity even when the reaction parameters are changed⁸.

The formation of toluene and benzene is the result of the interaction of ethylbenzene with acidic and basic sites of the catalyst. According to Wang *et al.*, strong acidic sites abstract α -hydrogen of ethylbenzene facilitating the formation of benzene³⁶. The formation of toluene can be justified with the help of the conclusion by Krause that strong basic sites preferably abstract β -hydrogen from ethylbenzene resulting in the formation of toluene³⁷. The selectivity of toluene is reduced due to vanadia incorporation. This agrees with the observation of electron acceptor adsorption studies that basic sites are decreasing as a result of vanadia impregnation.

Table 3—Dehydrogenation of ethylbenzene over La / V system [Reaction conditions: Reaction temperature=475 °C; feed rate=6 ml/h; catalyst=2 g; time on stream=1 h.]

Catalyst	Conversion (%)	Selectivity (%)			
		Styrene	Toluene	Benzene	C-oxides
La_2O_3	6.2	78.3	10.4	2.5	8.8
La3	6.5	82.3	8.8	2.3	6.6
La7	7.3	86.6	6.4	2.3	5.3
La11	7.2	85.3	5.6	2.7	6.4
La15	7.8	87.2	5.8	2.6	4.4
Dy3	6.5	85.0	5.0	4.0	6.0
Dy7	5.5	90.9	4.5	2.7	1.9
Dy11	5.7	91.2	4.3	2.2	2.1
Dy15	6.8	91.7	2.2	2.6	3.3

In oxidative dehydrogenation of ethylbenzene, one of the most probable mechanisms consists of the abstraction of 'H' from the ethylbenzene by the lattice oxygen to form styrene and the reoxidation of the catalyst by gas phase oxygen³⁸. Similar conclusions regarding the mechanism have been reached by Tagawa *et al.*³⁹. To get an insight to the reaction pathway, the reaction was carried out in the absence of air (Table 3). The fact that the catalytic activity and percentage conversion were significantly reduced under non oxidative conditions, pointed out to the role of gaseous oxygen in the reaction. Reason for the reduced conversion may be the reduction of the catalyst. The formation of styrene reduces the catalyst system and the possibility of reoxidation is limited under non-oxidative conditions. The presence of air increases conversion, which indicates that the presence of gaseous oxygen favours the redox operation of the catalyst by supplying oxygen needed for hydrogen abstraction by reoxidising the catalyst. Mars and van Krevelen mechanism may be operating here which can be represented as,



where [O] is the lattice oxygen and [] is the lattice vacancy.

Besides, deposition of carbonaceous materials is also another factor, which leads to poisoning of active sites.

The selectivity towards styrene formation is increased under nonoxidative reaction conditions. High styrene selectivity in the absence of air must be due to the absence of gaseous oxygen. In the presence of external oxygen supply, the oxygen adsorbed at the active sites may be causing the complete oxidation of the adsorbed hydrocarbons. Similar observations are reported in some other systems. A reduction of styrene selectivity in presence of gaseous oxygen is reported by Chang *et al.*⁸. This is in agreement with the conclusion of a kinetic study on ethylbenzene conversion over a V-Mg-O catalyst that surface adsorbed oxygen is active in the combustion of hydrocarbon⁹. A similar reduction for the selectivity of the dehydrogenation product in the case of butene by gaseous oxygen has been reported on iron oxide⁴⁰. It can be seen that pure lanthana is highly selective towards styrene in non-oxidative reaction conditions. This can be accounted for like this. The complete oxidation of the hydrocarbons in the presence of adsorbed gaseous oxygen may be predominant in case of pure rare earth oxide. Hence, when compared to

the reaction in presence of air, La₂O₃ exhibited higher selectivity in non-oxidative conditions (Table 3). And it can be tentatively suggested that in the absence of external air, the redox sites created by vanadia on the surface is less active. This explains the nearly constant values of conversion in dehydrogenation in the absence of air.

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